

PALLADIUM PLATING FOR ELECTRONIC APPLICATIONS

SOBHA JAYAKRISHNAN and S R NATARAJAN

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

[Received: 1988 July; Accepted: 1988 July]

Palladium has been found to be a viable alternative to gold for contact surfaces in the electronic industry on account of its low cost, good resistance to corrosion and tarnishing, good solderability and good electrical conductivity. The present paper deals with the palladium bath performance, deposit characteristics and bath stability.

Key words: Palladium plating, electronic industry, electroplating

INTRODUCTION

Electrodeposited gold has been the ideal contact material for the electronic industry on account of its desirable characteristics like low and stable electrical contact resistance, excellent resistance to corrosion and tarnish and very good solderability. The replacement of gold with other materials is receiving considerable attention in recent years especially because of the rapidly increasing bullion cost. Among the various substitutes, namely rhodium, ruthenium, palladium, silver etc. suggested [1,2] for replacing gold in electrical contacts, palladium and its alloys appear to be satisfactory alternatives. The economic advantage of substituting gold with palladium is clear from the fact that its cost is approximately one third that of gold and its density is about half that of the latter.

Various electrolytes [3,4] have been proposed for electroplating palladium. The available literature shows however that electrolytes of ammine complexes offer distinct advantages in producing satisfactory deposits. It is reported [5,6] that ductile coatings of palladium can be produced from ammine chloride and bromide baths. A study of the preparation of these plating baths and some of their plating characteristics has been reported earlier [7].

The present paper deals with the behaviour of a palladium bath based on tetraamminopalladous bromide under varying operating conditions.

EXPERIMENTAL

The ammine bromide complex was prepared starting from palladium chloride through the intermediate preparation of palladium bromide. A concentrated solution of the complex was prepared (for details see Ref. 7) and analysed for its exact palladium concentration. This was used to prepare the following plating baths:

Palladium as $\text{Pd}(\text{NH}_3)_4 \text{Br}_2$ (g. L⁻¹) 5-25
Ammonium bromide (g. L⁻¹) 40
Ammonium hydroxide | As required
Hydrobromine acid |

Electrodeposition studies were carried out with platinum as anode and copper (both of 4 cm x 1 cm) as cathode. Deposits of comparable thickness (10 μm) were produced and nature of deposits examined visually. Cathode current efficiencies were assessed by gravimetry. The effects of varying metal content, bath pH, temperature and cathode current efficiency were examined.

The deposits obtained were subjected to tests for evaluation of their porosity, internal stress and micro hardness. The porosity was determined by cadmium sulphide paper test [8], the stress by Hoar and Arrowsmith method [7] and the micro hardness by the Vickers indentation method. The surface structure of deposits was studied by means of Scanning Electron Microscope.

RESULTS AND DISCUSSION

Effect of varying metal concentration

The metal concentration was varied within the range 5-25 g. L⁻¹. The deposits were found to be smooth and adherent with a dull white appearance with 10-20 g. L⁻¹ metal in solution. The influence of metal concentration on cathode efficiency is represented in Fig.1. Curve 1 shows that whereas the current efficiency is low at metal contents below 10 g. L⁻¹, it increases with palladium concentration to a high level up to 15 g. L⁻¹ and remains nearly constant thereafter.

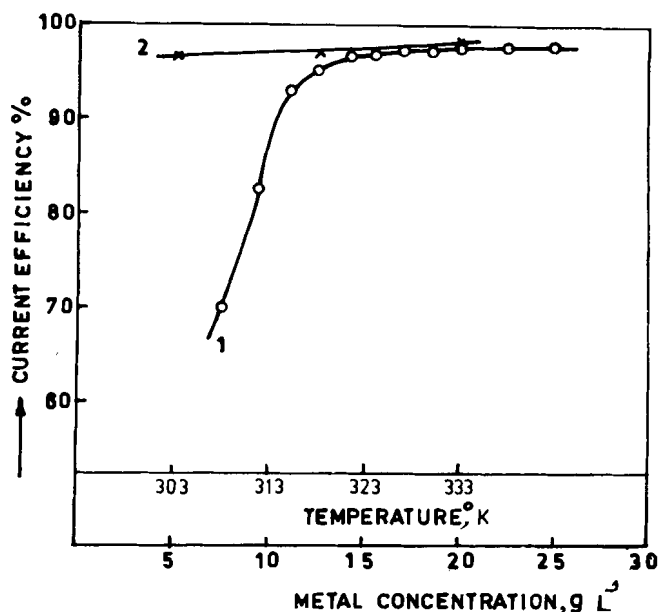


Fig. 1: Effect of metal concentration (curve 1) and temperature (curve 2) on the cathode current efficiency

Effect of temperature

An increase in temperature renders the deposit darker with no appreciable increase in current efficiency, (curve 2 in Fig. 1). Also operation at higher temperatures is beset with solution evaporation and loss of ammonia leading to fall in bath pH.

Effect of current density

Current density was varied in the range $0.5 - 3.0 \text{ A. dm}^{-2}$ for palladium solution. The deposits were greyish white below 0.5 A. dm^{-2} , rough and dark grey above 2.5 A. dm^{-2} and black, powdery and nonadherent at still higher current densities. As shown in Fig. 2 (curve 1), there is an appreciable loss of efficiency at current densities higher than 2.0 A. dm^{-2} .

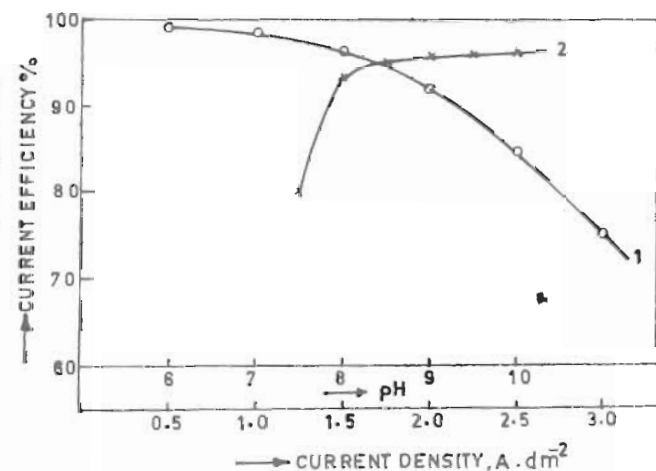


Fig. 2: Effect of current density (curve 1) and pH (curve 2) on the cathode current efficiency

Effect of solution pH

The optimum pH was found to be in the range 8.5 to 10.0. Though the deposit properties were not affected by operation even at pH 11, the rapid loss of ammonia by evaporation from this highly ammoniacal solution was a problem in operation. At a pH less than 8.5, precipitation at the platinum anode was observed interfering with bath stability, and causing roughness of deposits. All this can be due to the evolution of bromine at the anode which converts the tetra ammino complex to the insoluble diammino bromide under the highly acidic conditions prevailing there. The effect of pH on cathode current efficiency is indicated in Fig. 2, (curve 2) showing that operation in the pH range 8.5 - 10.0 is possible without much change in efficiency.

Based on the above studies, it is concluded that smooth, adherent, dull white palladium deposits can be plated from tetra ammino palladium dibromide bath under the following conditions:

Metal concentration (g. L ⁻¹)	15 - 20
Temperature (K)	303 - 313
Cathode current density (A. dm ⁻²)	0.5 - 1.5
pH	8.5 - 10.0

Electrodeposit characterisation

The deposits obtained under the optimised conditions were found to have the following characteristics:

Internal stress (at $5 \mu\text{m}$)	7.0 kg/mm ²
Micro hardness (25 gm load) ($25 \mu\text{m}$)	140 V H N
Cathode current efficiency	96%

The test on deposit porosity showed that deposits of more than $5-6 \mu\text{m}$ thickness were pore free. No cracking was observed in deposits even when applied in $25-30 \mu\text{m}$ thickness. In Fig. 3a and 3b are included Scanning Electron Micrographs (SEM) of $25 \mu\text{m}$ palladium deposits produced from the above bath at 303K and 333K.

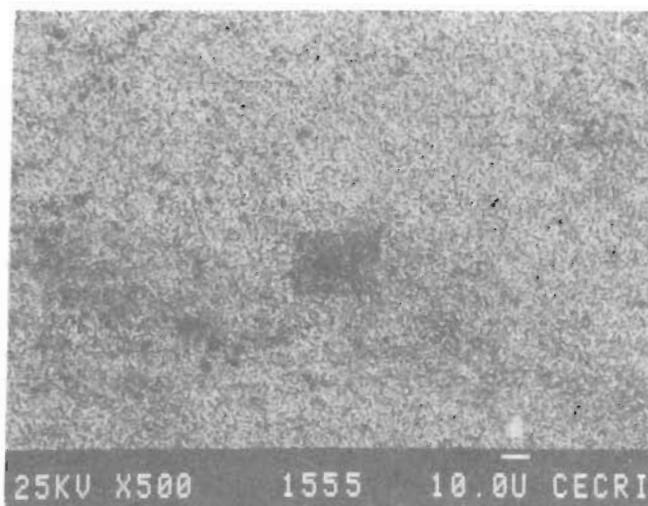


Fig. 3-a: Scanning electron micrograph of palladium deposit ($25 \mu\text{m}$) obtained from the bath at 303K

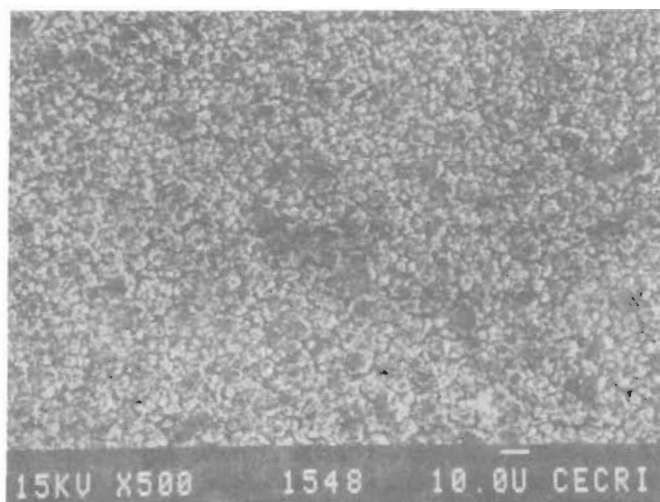


Fig. 3-b: Scanning electron micrograph of palladium deposit ($25 \mu\text{m}$) obtained from the bath at 333K

respectively. The SEMs (Fig. 4a-4d) which correspond to deposits from the optimised bath, show a gradual increase in grain size when the plating thickness is increased from $1\mu\text{m}$ to $10\mu\text{m}$ and thereafter it is not much affected.

where some serious contamination of the bath was suspected, the precipitation of the diammine as bromide followed by filtration, thorough washing and redissolution of the precipitate was found to be effective in renovating the bath.

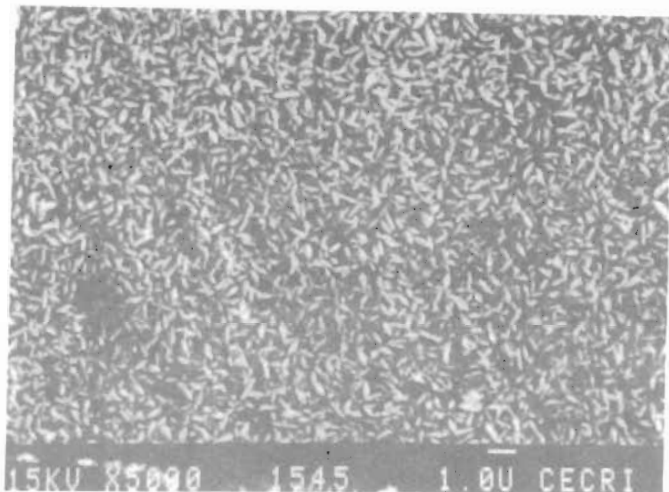


Fig. 4a: Scanning electron micrograph of deposits with thickness $1\mu\text{m}$

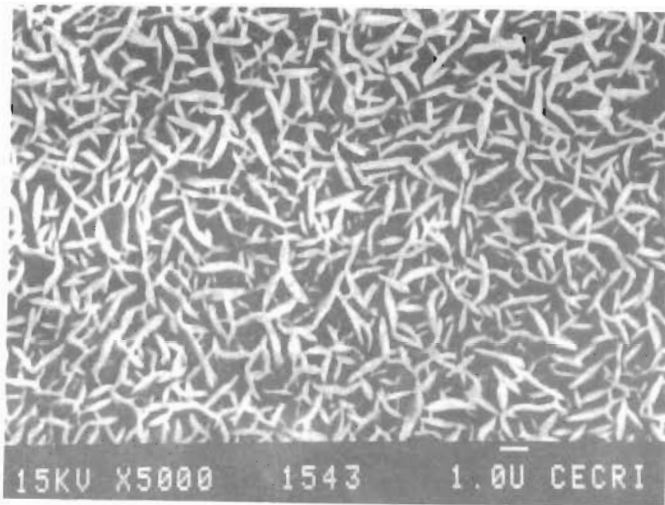


Fig. 4b: Scanning electron micrograph of deposits with thickness $5\mu\text{m}$

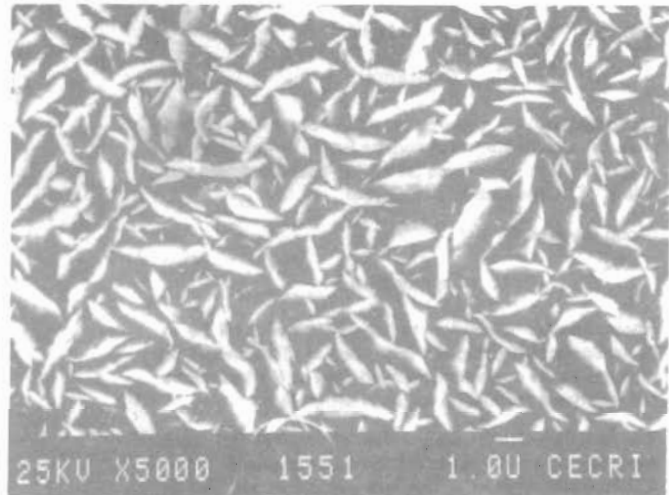


Fig. 4c: Scanning electron micrograph of deposits with thickness $10\mu\text{m}$,

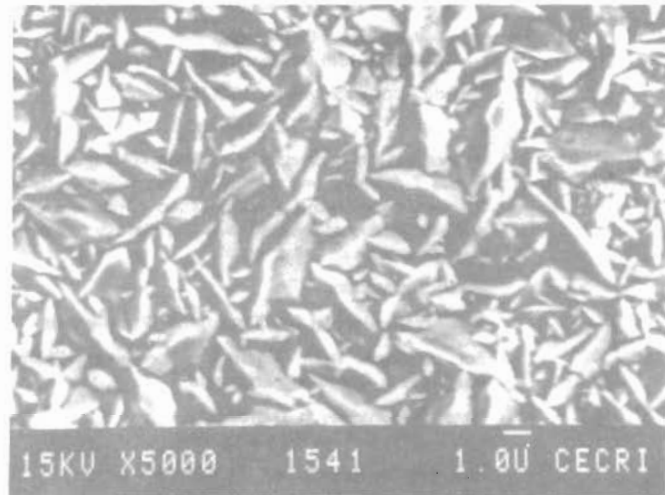


Fig. 4d: Scanning electron micrograph of deposits with thickness $25\mu\text{m}$

Bath stability

The bath was found to be quite stable provided its pH was maintained well above 6 or 7 at which palladium complex would get precipitated. No problem was experienced with continuous use of the bath. Frequent bath analysis and replenishment was required as the anode used was an insoluble one. The replenishment was effected using a solution concentrate of the complex salt. In cases

CONCLUSION

The palladium plating bath with palladium present as tetra ammine palladous bromide complex has been found to be capable of producing smooth, adherent and pore-and-crack-free palladium deposits.

REFERENCES

1. R G Baker, *Plating and Surf Finish*, 73 (1986) 40
 2. H M Smith, *Metal Finish*, 81 - 4 (1983) 63
 3. J Fischer and D E Weimer, *Precious Metal Plating*, Robert Draper Ltd, Teddington (1984)
 4. *Metal Finishing Guide Book and Directory*, Metals and Plastics Publications Inc, New Jersey, (1986)
 5. H C Angus, *Trans Inst Metal Finish*, 44 (1966) 41
 6. J M Steven; *Ibid*, 64 (1986) 41
 7. Sobha Jayakrishnan and S R Natarajan, *Metal Finish*, 86-2, (1988) 81.
 8. F H Reid, *Plating*, 52 (1965) 531
- 